

# Electronic structure properties and BCS superconductivity in $\beta$ -pyrochlore oxides: $\text{KOs}_2\text{O}_6$

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We report a first-principles density-functional calculation of the electronic structure and properties of the recently discovered superconducting  $\beta$ -pyrochlore oxide  $\text{KOs}_2\text{O}_6$ . We find that the electronic structure near the Fermi energy  $E_F$  is dominated by strongly hybridized Os-5d and O-2p states. A van Hove singularity very close to  $E_F$  leads to a relatively large density of states at  $E_F$ , and the Fermi surface exhibits strong nesting along several directions. These features could provide the scattering processes leading to the observed anomalous temperature dependence of the resistivity and to the rather large specific heat mass enhancement we obtain from the calculated density of states and the observed specific heat coefficient. An estimate of  $T_c$  within the framework of the BCS theory of superconductivity taking into account the possible effects of spin fluctuations arising from nesting yields the experimental value.

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Transition metal (TM) oxides are of intrinsic interest in physics because of the very rich phenomenology they exhibit due to electron correlations, ranging from metal-insulator transitions to colossal magnetoresistance and high critical temperature superconductivity. TM oxide compounds with the pyrochlore structure have long been studied and have found many applications thanks to their diverse electronic properties,<sup>1</sup> but it is not until recently that superconductivity was found in one such a material, namely  $\text{Cd}_2\text{Re}_2\text{O}_7$ .<sup>2,3</sup> Although its superconducting critical temperature turned out to be low ( $T_c \simeq 1$  K), it was an important discovery because it opened research in this area to a new class of materials. Very recently, superconductivity was reported in  $\text{KOs}_2\text{O}_6$ ,<sup>4,5</sup> a so-called  $\beta$ -pyrochlore, with a  $T_c$  of 9.6 K. More reports of superconductivity in the same family of compounds have followed at a rapid pace, with superconductivity being observed in  $\text{RbOs}_2\text{O}_6$  ( $T_c = 6.3$  K)<sup>6,8</sup> and in  $\text{CsOs}_2\text{O}_6$  ( $T_c = 3.3$  K),<sup>10</sup> adding to the interest in these materials.

The discovery of superconductivity in the  $\beta$ -pyrochlores raises, of course, the question of the underlying mechanism. While the mechanism in  $\text{Cd}_2\text{Re}_2\text{O}_7$ , an  $\alpha$ -pyrochlore,<sup>10</sup> can be understood within the weak-coupling Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity,<sup>11</sup> Hiroi and co-workers have suggested<sup>5</sup> from the outset that  $\text{KOs}_2\text{O}_6$  is an unconventional superconductor, with the pairing mediated by spin fluctuations.<sup>7</sup> On the other hand, Batlogg and co-workers suggested<sup>8</sup> that  $\text{RbOs}_2\text{O}_6$  could be a conventional BCS-type superconductor, and recent pressure effects measurements appear to bring further support to their conclusions.<sup>9</sup> Given the close similarity between these two compounds, it seems unlikely that their superconductivity has a different origin. Clearly, a careful study of the electronic structure of these materials may shed light on the superconductivity mechanism.

In this work, we focus on  $\text{KOs}_2\text{O}_6$  and carry out a self-consistent first-principles density-functional calculation of its electronic structure, using a newly paral-

lelized implementation<sup>12</sup> of the full-potential linearized augmented plane wave (FLAPW) method.<sup>13</sup> Our calculations are made within the Perdew, Burke, and Ernzerhof generalized gradient approximation (GGA)<sup>14</sup> to the exchange-correlation potential and include the spin-orbit coupling (SOC) term in the Hamiltonian. Our results show that the electronic structure near the Fermi energy ( $E_F$ ) is dominated by strongly hybridized Os-5d and O-2p states. There is a van Hove singularity (vHS) very close to  $E_F$ , leading to a relatively large density of states (DOS) at  $E_F$ , and the Fermi surface shows strong nesting along several directions. These features could provide the scattering processes leading to the reported<sup>4,5</sup> anomalous temperature dependence of the resistivity above  $T_c$ , and to the rather large specific heat mass enhancement we obtain from the calculated DOS and the measured low temperature specific heat coefficient.<sup>5</sup> We estimate the  $T_c$  within the BCS framework and are able to obtain the experimental value if we take into account the possible effects of spin fluctuations arising from nesting.

$\text{KOs}_2\text{O}_6$  crystallizes in a cubic structure with space group  $Fd\bar{3}m$ , and has 18 atoms per unit cell: two K (8b), four Os (16c), and twelve O (48f).<sup>4</sup> The structure has an internal parameter  $x$ , that fixes the position of the oxygen atoms. The experimental lattice constant recently given by Yonezawa and co-workers is  $a = 10.101$  Å,<sup>5</sup> but no value for the  $x$  parameter has yet been reported. We have optimized variationally both the lattice constant and the internal parameter, obtaining  $a = 10.298$  Å, which differs by 1.95% from the experimental value, and  $x = 0.316$ . The latter can be compared with the value of  $x = 0.315$  recently reported for the related superconducting pyrochlore  $\text{RbOs}_2\text{O}_6$  by Brühwiler and collaborators.<sup>8</sup> Each Os atom is octahedrally coordinated by six O atoms, with O-Os-O angles of 88.66° and 91.34° (compare with 88.85° and 91.15°, respectively, for  $\text{RbOs}_2\text{O}_6$ , reported in Ref. 8). Unlike the perovskite superconductors, in the pyrochlore oxides the transition metal-oxygen octahedra are not distorted. The Os-O distance we find is 1.94 Å

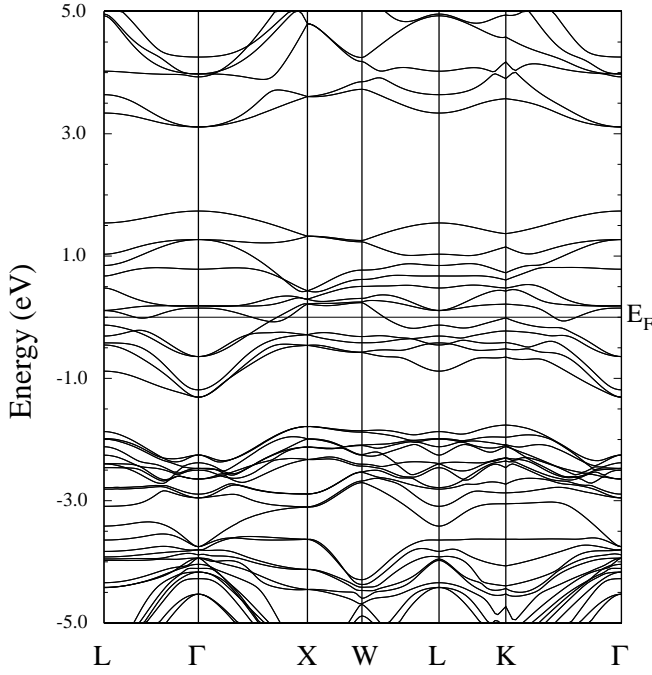


FIG. 1: Band structure of  $\text{KOs}_2\text{O}_6$ , calculated within the GGA for exchange and correlation and taking into account spin-orbit coupling self-consistently. The twelve bands around  $E_F$  arise from Os  $5d$  and O  $2p$  states. A saddle point near the center of the  $\Gamma L$  line causes a vHS very close to  $E_F$ .

(compare with, for example, the calculated<sup>15,16</sup> Ru-O distances of 1.93 Å and 2.061 Å in  $\text{Sr}_2\text{RuO}_4$ ). In  $\text{KOs}_2\text{O}_6$ , the pyrochlore lattice is formed by highly interconnected Os-O staggered chains, resulting in corner sharing tetrahedra, with the Os ions occupying the vertices. In Ref. 8, it is suggested that in the  $\beta$ -pyrochlore oxides, the transition TM-O-TM angle plays a role in defining the superconducting properties,<sup>8</sup> with smaller angles favoring higher critical temperatures. For  $\text{KOs}_2\text{O}_6$ , we find an Os-O-Os angle of  $139.16^\circ$ , which is indeed smaller than the reported angle of  $139.4^\circ$  for  $\text{RbOs}_2\text{O}_6$ .<sup>8</sup> There is currently not enough experimental information regarding  $\text{CsOs}_2\text{O}_6$  for comparison with this material.

The calculated energy bands along high symmetry directions in  $\mathbf{k}$ -space, within 5 eV from  $E_F$ , are shown in Fig. 1. There is a manifold of twelve states in the vicinity of  $E_F$ , with a bandwidth of 3 eV, separated by relatively large energy gaps above and below. Two bands cross the Fermi energy: the lower band cuts the  $\Gamma X$  and  $WL$  lines and gives rise to a hole-like Fermi surface sheet in the form of a tubular network; the upper band crosses  $E_F$  twice within the first Brillouin zone (cf. the  $\Gamma L$ ,  $\Gamma X$ , and  $\Gamma K$  lines), giving rise to two Fermi surface sheets. As will be illustrated below, this results in an electron-like closed shell centered at the  $\Gamma$  point. Of importance is the existence of a vHS very close to  $E_F$ , caused by a saddle point between the two sheets at  $\sim 0.015$  eV below the Fermi level, near the middle of the  $\Gamma L$  line.

The character of the bands near  $E_F$  is further ana-

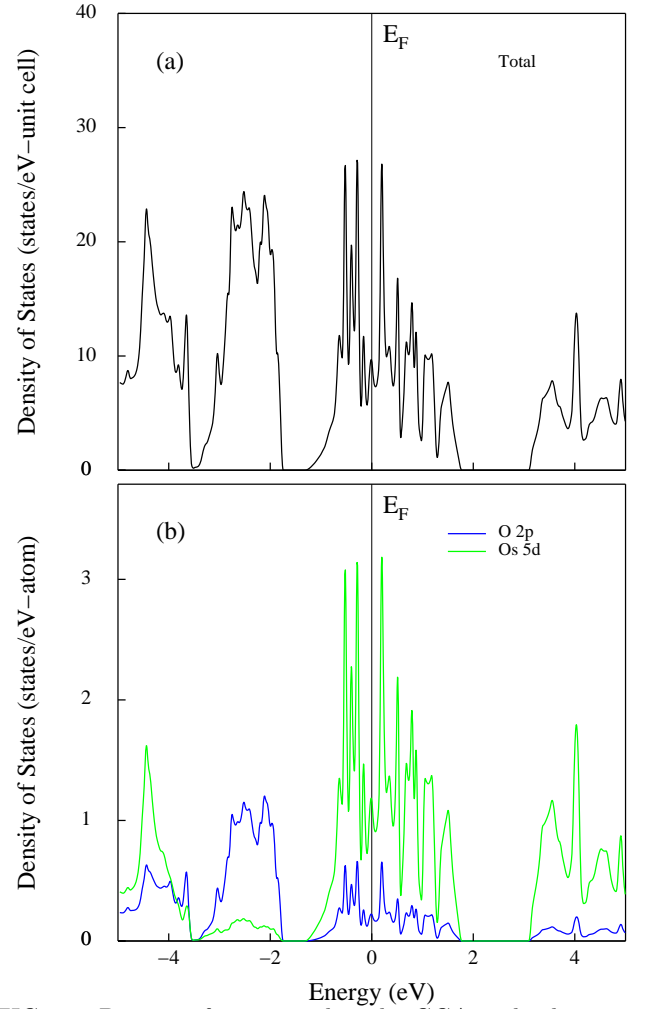


FIG. 2: Density of states within the GGA and taking into account spin-orbit coupling self-consistently. (a) Total DOS, showing a sharp peak very close to  $E_F$ . (b) Projected DOS of the O  $2p$  and Os  $5d$  states, on a per atom basis.

lyzed by examining the density of states (DOS). The total DOS, shown in Fig. 2(a), exhibits a peak very close to  $E_F$ , due to the vHS mentioned above. We point out that a precursor of the peak is already present, at a slightly lower energy, in a calculation without including spin-orbit coupling; the inclusion of the latter splits this peak, causes the saddle point, and pushes the higher peak closer to  $E_F$ . In Fig. 2(b) we show the partial DOS of the O  $2p$  and Os  $5d$  states, which are by far the dominant states in the energy range shown. As in previously studied oxide superconductors,<sup>15,16,17</sup> the TM and O states are strongly hybridized near  $E_F$ . The orbital character of the states near  $E_F$  is Os  $d\epsilon(xy, yz, zx)$  and O  $p\pi$ . This is clearly shown in Fig. 3, which presents a contour plot of the charge density in the  $(1\bar{1}0)$  plane for states lying within 0.027 eV below  $E_F$ .<sup>18</sup>

An important finding is that the Fermi surface shows strong nesting, in particular the shell-like sheets. Contour plots of the eigenenergies for the corresponding band along two different planes centered at the  $\Gamma$  point are

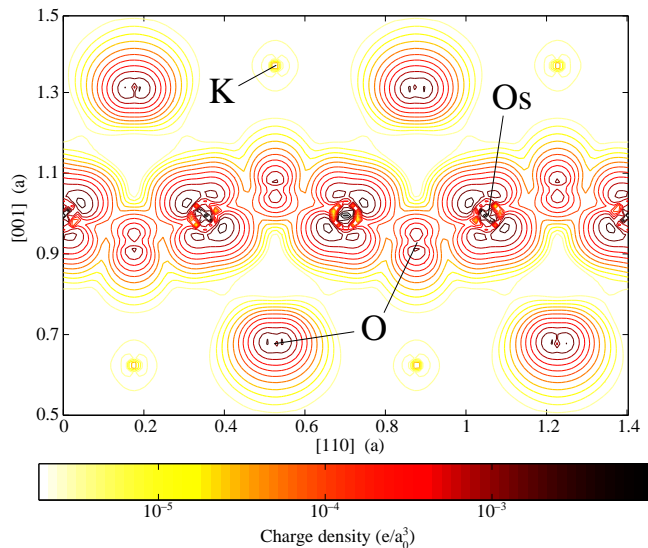


FIG. 3: Contour plot of the charge density in the  $(1\bar{1}0)$  plane for states lying within 0.027 eV below  $E_F$ . A staggered Os-O chain is clearly seen. The other oxygen ions in the plot belong to chains traversing the  $(1\bar{1}0)$  plane. As expected, the charge around the potassium ions is extremely weak.

given in Fig. 4. Figure 4(a) shows the contour plot for  $\mathbf{k}$  in the  $X\Gamma X$  plane, with strong nesting occurring for  $k \simeq 0.4 \, 4\pi/a$  and  $k \simeq 0.62 \, 4\pi/a$  along the  $\Gamma K$  directions. Similarly, Fig. 4(b) shows a contour plot for  $\mathbf{k}$  in the  $X\Gamma K$  plane, also showing strong nesting, in particular for  $k \simeq 0.64 \, 4\pi/a$  along  $\Gamma L$  directions.

Consider further some of the properties deduced from the electronic structure in relation to experiment. Firstly, the DOS at the Fermi level is relatively high,  $N(E_F) = 9.8$  states/eV-unit cell, yielding a Sommerfeld electronic specific heat coefficient  $\gamma = 5.78$  mJ/K<sup>2</sup> mol-Os. This is much lower than the experimental value of 19 mJ/K<sup>2</sup> mol-Os found by Hiroi and collaborators,<sup>5</sup> based on their estimation of the specific heat jump at  $T_c$  and the BCS weak-coupling relation  $\Delta C/\gamma T_c = 1.43$ . Thus, we find a very large specific heat mass enhancement  $\gamma_{\text{exp}}/\gamma_{\text{band}} \simeq 3.3$ , though it is still smaller than that of, e.g., Sr<sub>2</sub>RuO<sub>4</sub>, found to be 3.8 or more.<sup>15,16</sup> The above mass enhancement represents a rather high coupling constant,  $\lambda = 2.3$ . Given the relatively low  $T_c$  of KOs<sub>2</sub>O<sub>6</sub>, it appears that, besides electron-phonon, there is a very important electronic many-body contribution to the specific heat mass enhancement. Interestingly, Hiroi and co-workers noted in particular the unusual behavior of the measured resistivity as a function of temperature.<sup>4,5</sup> Data corresponding to single crystals are greatly desirable to advance further in this direction. Let us just point out here that, under appropriate conditions, deviations from conventional Fermi liquid behavior in two-dimensional systems can be caused by both vHS's near the Fermi energy<sup>19</sup> and by Fermi surface nesting,<sup>20</sup> due to the increased phase space available for electron-electron scattering.<sup>21</sup>

From the measured  $T_c = 9.6$  K, and using  $\Delta =$

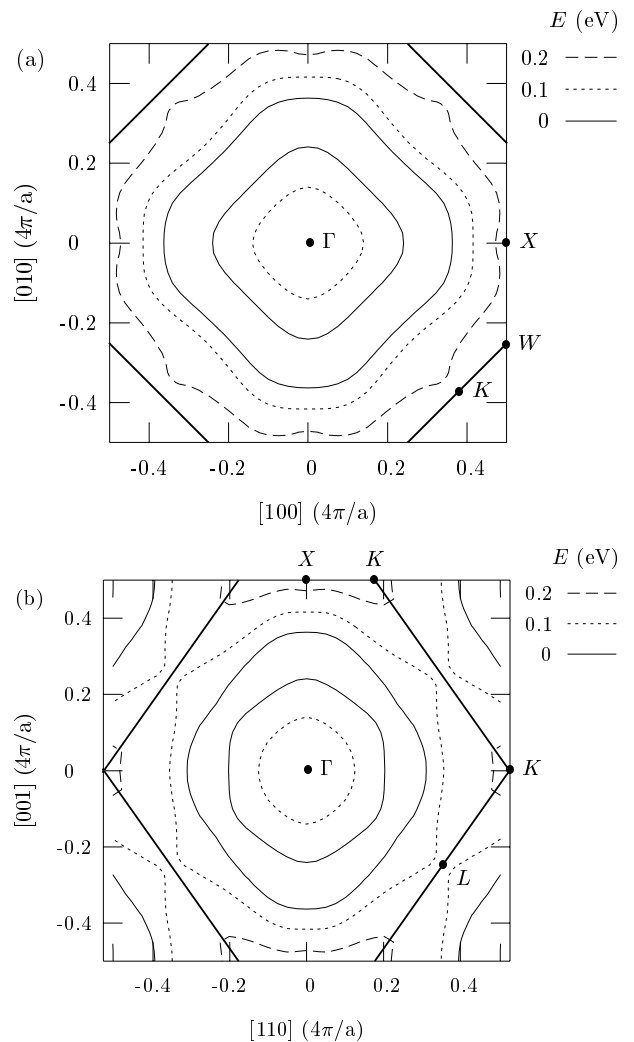


FIG. 4: Contour plots of the upper band crossing  $E_F$  (cf. Fig. 1) along two high symmetry planes.  $E = 0$  corresponds to  $E_F$ . The thick lines indicate the first Brillouin zone boundaries. (a) Plot for  $\mathbf{k}$  in the  $X\Gamma X$  plane. Extensive nesting occurs for  $\mathbf{k}$  along  $\Gamma K$ , with  $k \simeq 0.4$  and  $0.62 \, 4\pi/a$ . (b) Plot for  $\mathbf{k}$  in the  $\Gamma X K$  plane. Strong nesting occurs, e.g., for  $\mathbf{k}$  along  $\Gamma L$ , with  $k \simeq 0.64 \, 4\pi/a$ .

$1.76k_B T_c$ , the superconducting gap is calculated to be  $\Delta = 1.456$  meV. A calculation of the average Fermi velocity then allows us to readily estimate the BCS-Pippard coherence length  $\xi_0 = \hbar \langle v_F \rangle / \pi \Delta$ . We find  $\langle v_F \rangle = 1.47 \times 10^7$  cm/s, which yields  $\xi_0 = 212$  Å. This is an order of magnitude larger than the reported Ginzburg-Landau coherence length  $\xi = 30$  Å, obtained from the estimated upper critical field  $H_{c2}$ .<sup>5,22</sup> Thus, the so-called dirty limit would apply. Indeed, writing  $\xi^{-1} = \xi_0^{-1} + l^{-1}$ , with  $l$  the mean free path, yields an estimated value of  $l = 35$  Å. This relatively short value suggests again that strong scattering processes play an important role in the electronic properties of this material.

We estimate the McMillan-Hopfield<sup>23,24</sup> electron-phonon coupling constant  $\lambda_{\text{ep}}$ , for which the

constituent-weighted average can be written  $\lambda_{\text{ep}} = \sum_i w_i \eta_i / M_i \langle \omega^2 \rangle$ .<sup>25</sup> Here, the spherically averaged Hopfield parameters,  $\eta$ , were calculated in the crude rigid-muffin-tin approximation, with<sup>26</sup>

$$\eta = 2N(E_F) \sum_l (l+1) M_{l,l+1}^2 \frac{f_l f_{l+1}}{(2l+1)(2l+3)}, \quad (1)$$

where  $f_l = N_l(E_F)/N(E_F)$  is a relative partial DOS and  $M_{l,l+1} = -\phi_l \phi_{l+1} [(D_l - l)(D_{l+1} + l + 2) + (E_F - V)R^2]$  is an electron-phonon matrix element. The quantities entering the latter are the logarithmic derivatives ( $D_l$ ) and the partial wave amplitudes ( $\phi_l$ ), both evaluated at  $E_F$  and at the muffin-tin radius ( $R$ );  $V$  is the one-electron potential at  $R$ . The average phonon frequency can be estimated by  $\langle \omega^2 \rangle^{1/2} = 0.69 \Theta_D$ . There is currently no reported  $\Theta_D$  for  $\text{KOs}_2\text{O}_6$ , but Brühwiler and co-workers did such measurements for  $\text{RbOs}_2\text{O}_6$ .<sup>8</sup> Under the assumption that the values of  $\Theta_D$  fall in the same range for both materials, we take  $\Theta_D = 240$  K, and obtain  $\lambda_{\text{ep}} = 1.4$ . As expected, this value is well below the total  $\lambda$  obtained from the specific heat mass enhancement discussed above.<sup>27</sup>

To estimate  $T_c$ ,<sup>28</sup> we use the Allen and Dynes modification of the McMillan equation,<sup>23,29</sup> including an effective

electron-spin interaction coupling constant  $\mu_{\text{sp}}$ ,<sup>30</sup> i.e.,

$$T_c = \frac{\langle \omega^2 \rangle^{1/2}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda_{\text{ep}} + \mu_{\text{sp}})}{\lambda_{\text{ep}} - (\mu^* + \mu_{\text{sp}})(1 + 0.62\lambda_{\text{ep}})} \right]. \quad (2)$$

The so-called Coulomb pseudopotential  $\mu^*$  can be estimated from the DOS at  $E_F$ ,<sup>30</sup> and in our case is  $\mu^* = 0.09$ . On the other hand, there is no simple expression for  $\mu_{\text{sp}}$ . If  $\mu_{\text{sp}} = 0$  we find  $T_c = 18$  K. Strong spin fluctuations,<sup>31</sup> with a coupling constant  $\mu_{\text{sp}} = 0.13$  would yield the experimental value  $T_c = 9.6$  K. As an estimate, from our DOS we have calculated the Pauli paramagnetic susceptibility, finding  $\chi_{\text{band}} = 1.58 \times 10^{-4}$  cm<sup>3</sup>/mol. From Ref. 5, we estimate the experimental value at  $T = 0$  to be  $\chi_{\text{exp}} \simeq 4 \times 10^{-4}$  cm<sup>3</sup>/mol, which yields an enhancement ratio  $\chi_{\text{exp}}/\chi_{\text{band}} = 2.53$ . Thus, strong spin fluctuations may indeed play an important role due to the significant nesting of the Fermi surface.

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- <sup>28</sup> A more rigorous estimation of  $\lambda$  and of  $T_c$  may require a more elaborate approach than the one adopted here, due to the peak in the DOS very close to  $E_F$ . See, e.g., E. Cappelluti and L. Pietronero, Phys. Rev. B **53**, 932 (1996).
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